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The thermodynamics of the carbonate system in seawater

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Abstract—The apparent constants (K_i') for the ionization of carbonic acid in seawater at various salinities (S, ‰) have been fit to equations of the form

$$\ln K_i' = \ln K_i + A_i S^{1/2} + B_i S$$

where K_i is the thermodynamic ionization constant in water, A_i and B_i are adjustable parameters. The temperature dependence (TK) of K_i, A_i and B_i were of the form, $a_0 + a_1/T + a_3 \ln T$. Equations of similar forms have been used to analyze the ionization constants for water and boric acid and the solubility product of calcite in seawater. The effect of pressure on the apparent constants (K_i^P/K_i^0) have been fit to equations of the form

$$\ln (K_i^P/K_i^0) = -(\Delta V P + 0.5\,\Delta K\,P^2)/RT$$

where the volume (ΔV) and compressibility (ΔK) changes are polynomial functions of temperature. The equations generated for various acids in seawater have been used to examine the carbonate system in seawater. Equations relating the NBS and Tris pH scales have been derived as well as equations of pH as a function of temperature and pressure. The equations from HANSSON (1972, Ph.D. Thesis, University of Göteborg, Sweden) and MEHRBACH *et al.* (1973, *Limnol. Oceanogr.* **18**, 897–907) have been used to examine the components of the carbonate system. At a fixed total alkalinity and total carbon dioxide, differences of ± 0.01 m-equiv kg^{-1} in HCO_3^- and CO_3^{2-} were found; however, the $[CO_2]$ and P_{CO_2} are nearly the same. The contribution of borate ion, $B(OH)_4^-$ determined from the equations of HANSSON (1972, Ph.D. Thesis, University of Göteborg, Sweden) and LYMAN (1957, Ph.D. Thesis, University of California, Los Angeles) differ by ± 0.01 m-equiv kg^{-1} for waters with the same salinity and temperature.

INTRODUCTION

RECENTLY we had a need to use apparent constants for boric and carbonic acid in seawater to determine the parameters of the carbonate system in the Mediterranean Sea (MILLERO *et al.*, 1978, 1979). An examination of the equations presently available (EDMOND and GIESKES, 1970; TAKAHASKI *et al.*, 1970; ALMGREN *et al.*, 1975; MEHRBACH *et al.*, 1973) for the salinity and temperature dependence of the apparent constants revealed a wide discrepancy in the form and number of parameters used. EDMOND and GIESKES (1970) have reviewed the earlier work of LYMAN (1957) and BUCH (1932, 1933, 1938, 1951). In recent years two independent studies on the carbonate system have appeared (HANSSON, 1972; MEHRBACH *et al.*, 1973). The measurements of HANSSON (1972) are based on a Tris buffer scale (HANSSON, 1973) while the measurements of MEHRBACH *et al.* (1973) are based on the NBS buffer scale (BATES, 1964).

The purpose of the present paper is to thoroughly analyze the measurements of these workers and to provide a statistically valid representation of the apparent constants as a function of salinity, temperature and pressure.

EQUATIONS FOR APPARENT CONSTANTS AT ONE ATMOSPHERE

Two general criterion were used to examine the salinity and temperature dependence of the apparent constants for the ionization of acids in seawater: (1) the temperature derivatives of the constants should yield reliable thermodynamic quantities (ΔH and ΔCp, enthalpies and heat capacities); (2) the equations should be extrapolated to pure water when the salinity goes to zero. As shown by CLARK and GLEW (1966) reliable thermodynamic functions can be derived from equilibrium constants (K_i) by using an equation of the form (TK)

$$\ln K_i = A + B/T + C \ln T + DT + ET^2 + \ldots \quad (1)$$

where A, B, C, etc., are adjustable parameters. The differentiation of eqn (1) with respect to temperature gives

$$\Delta H_i^\circ = RT^2(\delta \ln K_i/\delta T) = R[-B + CT + DT^2 + 2ET^3 + \ldots] \quad (2)$$

$$\Delta Cp_i^\circ = (\delta \Delta H_i/\delta T) = R[C + 2DT + 6ET^2 + \ldots] \quad (3)$$

To fit equilibrium constants for the ionization of acids over a temperature range of 50° only the A, B and C terms are necessary. HARNED and OWEN (1958) have used a slightly different equation

$$\ln K_i = A' + B'/T + C/T \quad (4)$$

to fit the ionization constants of acids in water. The statistical analysis of the ionization constants for carbonic acid in water shows that eqn (1) is slightly better than eqn (4) when three parameters are used.

Table 1. Parameters for the temperature dependence of the ionization of acids and the solubility of $CaCO_3$ in water[a]

	$\ln K_i' = A + B/T + C \ln T$				
Acid	A	$-B$	$-C$	σ	Reference
H_2O	148.9802	13847.26	23.6521	0.0014	HARNED and OWEN (1958)
$B(OH)_3$	148.0248	8966.90	24.4344	0.0027	OWEN (1934); MANOV *et al.* (1944)
H_2CO_3	290.9097	14554.21	45.0575	0.0024	HARNED and DAVIS (1943)
HCO_3^-	207.6548	11843.79	33.6485	0.0033	HARNED and SCHOLES (1941)
Solid					
Calcite	303.1308	13348.09	48.7537	0.035	JACOBSON and LANGMUIR (1974); BERNER (1976)
Aragonite	303.5363	13348.09	48.7537	0.05	BERNER (1976)

[a] Temperature range $0 \leq t°C \leq 50°$.

We have selected eqn (1) to fit the thermodynamic ionization constants of water (HARNED and OWEN, 1958), boric acid (OWEN, 1934; MANOV *et al.*, 1944), and carbonic acid (HARNED and SCHOLES, 1941; HARNED and DAVIS, 1943) in water from 0 to 50°C. The values of A, B and C (eqn 1) along with the standard errors are given in Table 1. Values of $\Delta H°$ and $\Delta Cp°$ for the ionization of H_2O, boric and carbonic acids at 25°C determined from eqns (2) and (3) are given in Table 2 along with directly measured values (HALE *et al.*, 1963; VANDERZEE and SWANSON, 1963; MILLERO, 1979a; LARSON and HEPLER, 1969; BERG and VANDERZEE, 1978). The agreement in the measured and calculated values of $\Delta H°$ are good. For $\Delta Cp°$ the agreement is not as good due to the errors in differentiating eqn (1) twice. As discussed by LARSON and HEPLER (1969) a more reliable temperature function for the ionization of acids can be obtained by integrating eqn (3) than the differentiation of eqn (1). As more reliable heat capacity data becomes available (for a recent review see MILLERO, 1979a), this should become possible in the near future. For the analysis of seawater data our representation of the temperature dependence of the ionization of acids are more than sufficient.

We have also fit the solubility product of calcite (JACOBSON and LANGMUIR, 1974 and BERNER, 1976) in water from 0 to 50°C to eqn (1). The coefficients A, B and C and the standard error are gi..n in Table 1. BERNER (1976) has recently measured the solubility of aragonite in water at 5 and 25°C. His results give $K_{sp}(\text{aragonite})/K_{sp}(\text{calcite}) = 1.48 \pm 0.14$ at 25°C and 1.43 ± 0.14 at 5°C. These values can be compared with the ratio calculated from the free energies of the two solids. LANGMUIR (1964) gives $\Delta G(\text{calcite} - \text{aragonite}) = -230 \pm 30\ \text{cal mol}^{-1}$ at 25°C, while CHRIST *et al.* (1974) give $-218 \pm 30\ \text{cal mol}^{-1}$ at 25°C and $-278 \pm 40\ \text{cal mol}^{-1}$ at 5°C. The value of $K_{sp}(\text{aragonite})/K_{sp}(\text{calcite}) = 1.46 \pm 0.08$ at 25°C obtained from these two studies are in good agreement with the measured value of BERNER (1976). At 5°C a value of 1.65 ± 0.12 is obtained from CHRIST *et al.* (1974) which is slightly higher than the experimental value of BERNER (1976). Within the error of the various estimates and measurements, we select the value of $K_{sp}(\text{aragonite})/K_{sp}(\text{calcite}) = 1.5 \pm 0.1$ from 5 to 25°C. Combining this estimate with the temperature coefficients, we have estimated the effect of temperature on the solubility of aragonite [the coefficient $A(\text{aragonite}) = A(\text{calcite}) + \ln(1.5)$ or 0.405].

The equation selected to represent the salinity dependence of apparent constants is given by

$$\ln K_i' = A' + B'S^{1/2} + C'S \tag{5}$$

This equation was arrived at by examining the value of K_i' of LYMAN (1957), HANSSON (1972), MEHRBACH *et al.* (1973), CULBERSON and PYTKOWICZ (1973), and INGLE *et al.* (1973, 1975) at a given temperature. Figures

Table 2. Values of $\Delta H°$ and $\Delta Cp°$ for the ionization of boric and carbonic acids in water at 25°C

	$\Delta H°$ (k cal mol^{-1})		$\Delta Cp°$ (cal mol^{-1} K^{-1})	
Acid	This study	Literature	This study	Literature
H_2O	13.50	13.34[a]	−47	−51[b]
$B(OH)_3$	3.34	3.37[c]	−49	−72[b]
H_2CO_3	2.23	2.19[d]	−90	−72[b]
HCO_3^-	3.60	3.51[d]	−67	−51[b]

[a] HALE *et al.* (1963); VANDERZEE and SWANSON (1963).
[b] Calculated from the heat capacity data tabulated by MILLERO (1979a).
[c] LARSON and HEPLER (1969).
[d] BERG and VANDERZEE (1978).

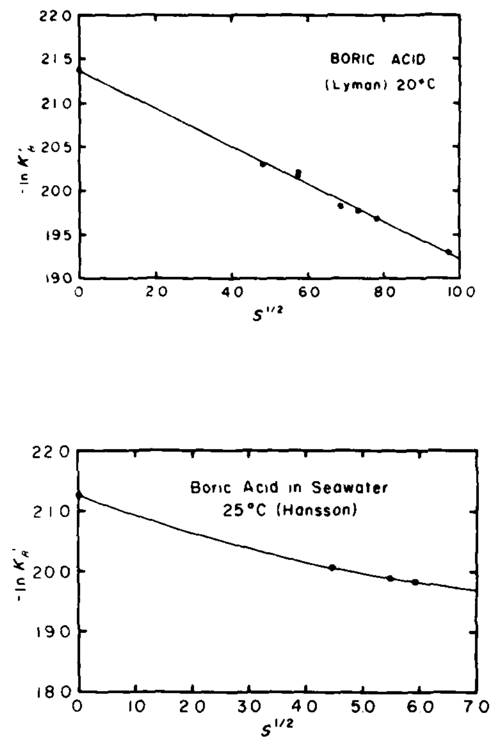

Fig. 1. The log of the apparent ionization constant of boric acid (K'_B) in seawater plotted versus the square root of the salinity.

1–5 show the plots of $\ln K'_i$ vs $S^{1/2}$ for the ionization of water, boric and carbonic acids, and the solubility of calcite. As is quite apparent from these plots the values of $\ln K_i$ for boric acid and H_2CO_3 from the work of Lyman and Mehrbach are linear functions of $S^{1/2}$ and the intercepts approach the thermodynamic values for pure water. For the ionization of H_2O, HCO_3^-, the solubility of calcite, and all the constants measured by HANSSON (1972) a second degree function is needed. The smooth curves in Figs 1–5 represent the least squares best fit of the data.

The temperature dependence of the terms in eqn (5) have been determined by fitting the directly measured apparent constants to the equation

$$\ln K'_i - \ln K_i = A'S^{1/2} + B'S \qquad (6)$$

where the parameters A' and B' have the same temperature form as $\ln K_i$ (the thermodynamic constant)

$$A' = a_0 + a_1/T + a_2 \ln T + \ldots \qquad (6a)$$

$$B' = b_0 + b_1/T + b_2 \ln T + \ldots \qquad (6b)$$

The parameters a_0 to a_i and b_0 to b_i for the ionization of H_2O, $B(OH)_3$, H_2CO_3, HCO_3^- and the solubility of $CaCO_3$ are given in Table 3 (along with the standard errors). The least squares computer program used to determine the adjustable parameters was the same as used in our equation of state work (formulated by Manny Mehr). Successive higher order terms were dropped until the standard error increased sufficiently to indicate by an F-test that the term was significant at the 95% level. The b_1 and b_2 terms were not needed for any of the systems studied. The b_0 term was not needed for the apparent constants of H_2CO_3 and $B(OH)_3$ measured on the NBS pH scale. The a_2 term was needed only for the ionization of water. It should be pointed out that Hansson's measured values of $\ln K'_B$ and $\ln K'_W$ at various temperatures were made only at $S = 35‰$.

The derived parameters represent the best statistically representation of the experimentally measured apparent constants. The validity of the constants for seawater diluted with pure water below 20‰ needs to be demonstrated experimentally.

The new carbonate results of MEHRBACH *et al.* (1973) and HANSSON (1972) have similar standard errors and appear to be more reliable than the earlier work of LYMAN (1957). The results of HANSSON (1972) for boric acid appear to be more reliable than the

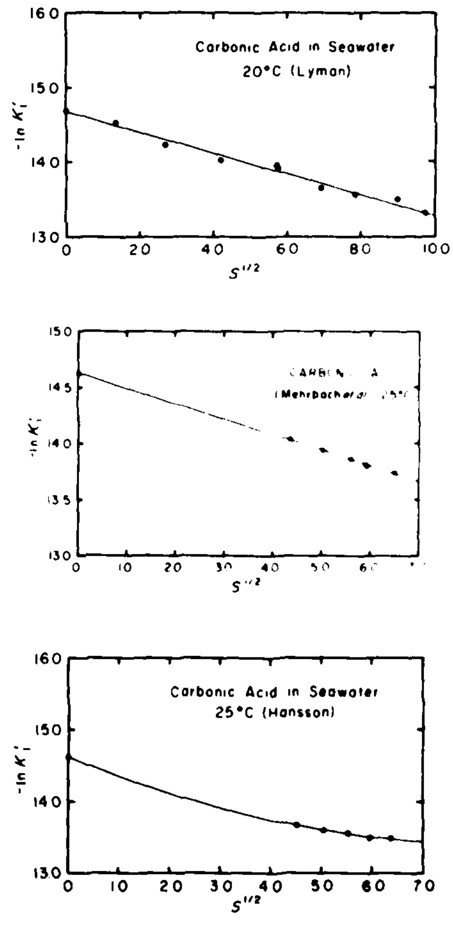

Fig. 2. The log of the apparent ionization constant of carbonic acid (K'_1) in seawater plotted versus the square root of the salinity.

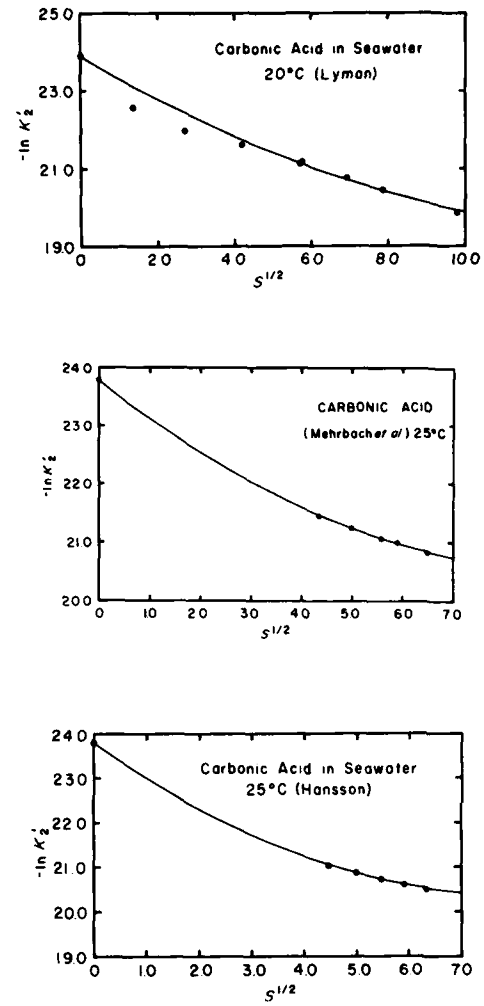

Fig. 3. The log of the apparent ionization constant of carbonic acid (K'_2) in seawater plotted versus the square root of the salinity.

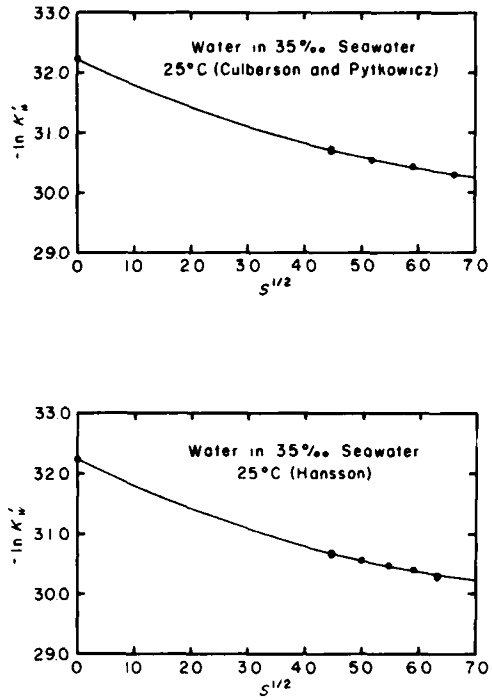

Fig. 4. The log of the apparent ionization constant of water (K'_W) in seawater plotted versus the square root of the salinity.

earlier work of LYMAN (1957). The pure water results of HANSSON (1972) and CULBERSON and PYTKOWICZ (1973) have similar standard errors.

The differences between the values of ln K_i obtained for the ionization of acids by various workers are shown in Figs 6–8. The smoothed values of ln K'_1 and ln K'_2 for carbonic acid from the results of Lyman and Mehrbach are within the sum of the standard errors of the fits (0.06 for ln K'_1 and 0.13 for ln K'_2) over the entire temperature and salinity range of the measurements. The differences in ln K'_1 at 25°C are quite small (0.004) and are randomly distributed. For ln K'_2 the differences are independent of temperature and nearly a linear function of salinity. The errors at high salinities are slightly larger (0.21 at $S = 40$) than the sum of the standard errors (0.13). From the comparisons with Hansson's work at these high salinities, Lyman's work appears to be in error.

The differences between the values of ln K'_W, ln K'_B, ln K'_1 and ln K'_2 obtained by Hansson and other workers at 25°C are given in Table 4. The values of ln K'_1 and ln K'_2 from Hansson's work are, respectively, 0.32 ± 0.03 and 0.37 ± 0.04 higher than the values of Lyman and Mehrbach *et al.* from 5 to 40‰ salinity. This is equivalent to a pH difference of 0.14–0.16 which is in good agreement with the measured values of 0.14–0.16 (HANSSON, 1973) and is related to the differences in the NBS and Tris buffer scales. For boric acid the differences in ln K'_B (between Hansson and Lyman) are 0.22 ± 0.04 which is 0.1 lower than expected. The recent measurements and calculations

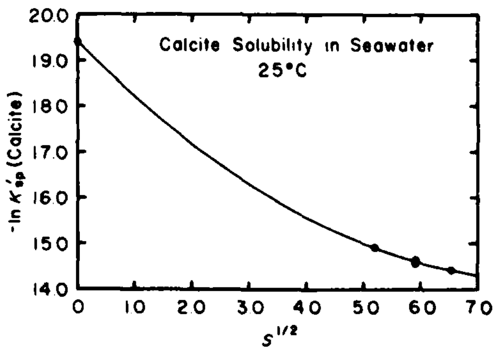

Fig. 5. The log of the apparent solubility constant of calcite (K'_{sp}) in seawater plotted versus the square root of the salinity.

Table 3. Parameters for the temperature dependence of apparent constants in seawater[a]

	$\ln K'_i - \ln K_i = (a_0 + a_1/T + a_2 \ln T)S^{1/2} + b_0 S$					
Solute	a_0	a_1	a_2	$b_0 10^2$	σ	Reference
H_2O	−97.9429	4149.915	14.8269	−2.3694	0.019	HANSSON (1972)
	−79.2447	3298.720	12.0408	−1.9813	0.020	CULBERSON and PYTKOWICZ (1973)
$B(OH)_3$	0.0473	49.10	—	—	0.049	LYMAN (1957)
	0.5998	−75.25	—	−1.767	0.008	HANSSON (1972)
H_2CO_3	−0.1110	74.02	—	—	0.053	LYMAN (1957)
	0.0221	34.02	—	—	0.007	MEHRBACH *et al.* (1973)
	0.5709	−84.25	—	−1.632	0.021	HANSSON (1972)
HCO_3^-	0.8925	−89.92	—	−1.530	0.097	LYMAN (1957)
	0.9805	−92.65	—	−3.294	0.033	MEHRBACH *et al.* (1973)
	1.4853	−192.69	—	−5.058	0.042	HANSSON (1972)
$CaCO_3$	1.6233	−118.64	—	−6.999	0.065	INGLE *et al.* (1973) INGLE (1975)

[a] In the salinity range $0 \leq S‰ \leq 40$ and temperature range $0 \leq t°C \leq 50$.

of BYRNE and KESTER (1974) at 25°C give a value of $\Delta \ln K_B = 0.27$ which is slightly higher (the earlier work of BUCH, 1933, gives $\Delta \ln K_B = 0.18$). These comparisons tend to indicate that the results of Hansson for boric acid are too low by 0.15 in $\ln K'_B$. Further studies are needed to clarify these differences.

The differences in $\ln K'_W$ of HANSSON (1972) and CULBERSON and PYTKOWICZ (1973) are 0.04 ± 0.01 at 25°C from 5 to 40‰ salinity which is nearly within the sum of the standard error of the fits (0.03).

Another method that can be used to examine the reliability of the apparent constants for the ionization of carbonic acid is to examine the ratio of K'_1/K'_2 (SKIRROW, 1975). Values of $\ln(K'_1/K'_2)$ obtained from the derived equation are shown at various salinities and temperatures in Fig. 9. The results of Lyman *et al.* are in good agreement and within the standard error of the measurements. Larger differences in $\ln(K'_1/K'_2)$ are found in the temperature dependence than in the salinity dependence.

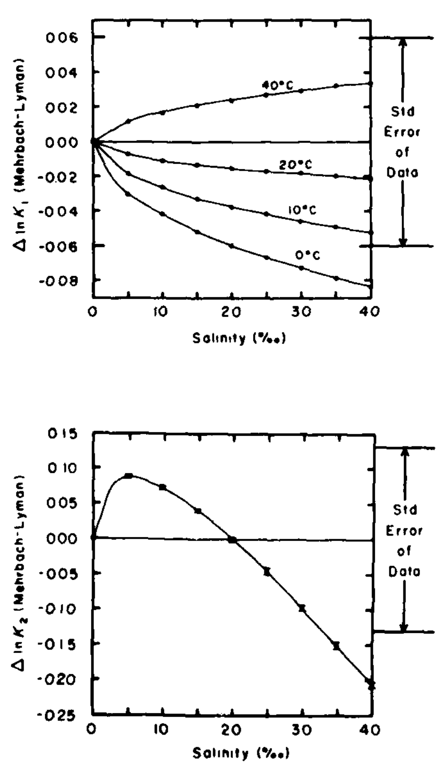

Fig. 6. Comparisons of the apparent ionization constants for carbonic acid obtained by MEHRBACH *et al.* (1973) and LYMAN (1957).

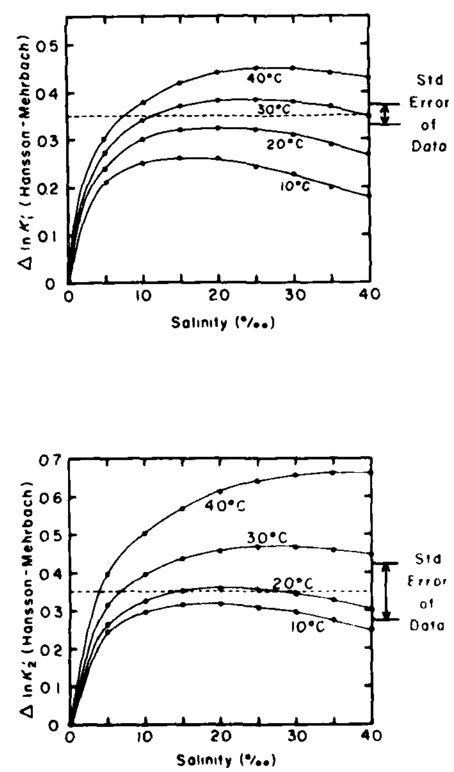

Fig. 7. Comparisons of the apparent ionization constants for carbonic acid obtained by HANSSON (1972) and MEHRBACH *et al.* (1973).

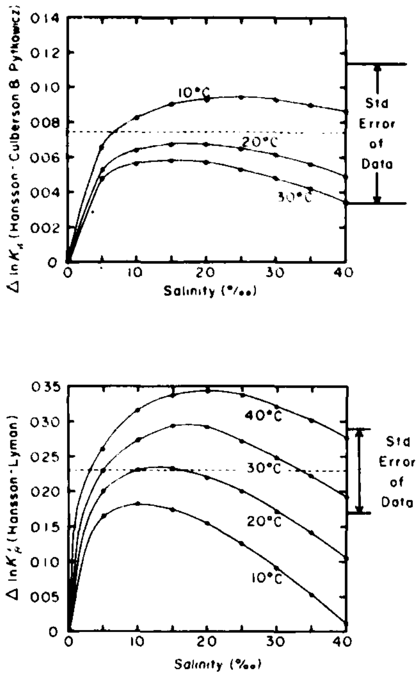

Fig. 8. Comparisons of the apparent ionization constants for boric acid and water obtained by HANSSON (1972), LYMAN (1957) and CULBERSON and PYTKOWICZ (1973).

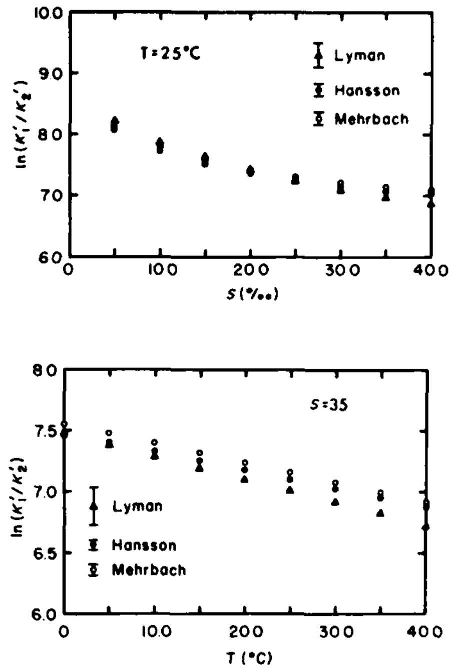

Fig. 9. Comparisons of the ratios of K_1' and K_2' for the ionization of carbonic acid obtained by LYMAN (1957), HANSSON (1972) and MEHRBACH *et al.* (1973).

The values of K'_{sp} for the solubility of calcite in seawater of INGLE *et al.* (1973, 1975) have been selected because their results cover a wide salinity and temperature range. These results have recently been confirmed at 5 and 25°C by the measurements of MORSE *et al.* (1979). The recent measurements of MORSE *et al.* (1979) yield values for the solubility of aragonite in seawater that are ~ 1.5 times their value for calcite. Thus, the equations for the effect of temperature and salinity on the solubility of calcite in seawater can also be used for the solubility of aragonite.

EQUATIONS FOR THE EFFECT OF PRESSURE ON APPARENT CONSTANTS

The equation selected to represent the effect of pressure on the apparent ionization constants of acids in seawater (CULBERSON and PYTKOWICZ, 1968) is

$$\ln (K_i^P/K_i^0) = -(\Delta V_i/RT)P + (0.5\,\Delta K_i/RT)P^2 \quad (7)$$

where ΔV_i and ΔK_i are the volume and compressibility change for the ionization. The values of ΔV_i and

Table 4. Comparisons of the values of ln K_i obtained by various workers for various acids in seawater at 25°C

S(‰)	Δ ln K'_W	Δ ln K'_B	Δ ln K'_1		Δ ln K'_2	
	a	b	b	c	b	c
5	0.049	0.214	0.264	0.259	0.386	0.290
10	0.059	0.252	0.323	0.318	0.447	0.359
15	0.061	0.259	0.347	0.344	0.453	0.391
20	0.060	0.252	0.353	0.354	0.433	0.404
25	0.057	0.235	0.349	0.353	0.396	0.405
30	0.052	0.212	0.336	0.344	0.345	0.398
35	0.046	0.183	0.318	0.329	0.285	0.384
40	0.040	0.150	0.295	0.309	0.218	0.365
	0.044 ± 0.007	0.22 ± 0.04	0.32 ± 0.03	0.32 ± 0.03	0.37 ± 0.08	0.37 ± 0.04

[a] HANSSON-CULBERSON and PYTKOWICZ.
[b] HANSSON-LYMAN.
[c] HANSSON-MEHRBACH *et al.*

Table 5. Coefficients for eqn (7a) and (7b)[a]

Solute	a_0	a_1	a_2	$a_3 10^3$	b_0	b_1	b_2	$\sigma(\ln K^P/K^0)$
$B(OH)_3$	29.48	−0.295	−0.1622	2.608	2.84	−0.354	—	0.0030
H_2CO_3	25.50	0.151	−0.1271	—	3.08	0.578	−0.0877	0.0043
HCO_3^-	15.82	−0.321	0.0219	—	−1.13	0.314	0.1475	0.0042
$CaCO_3$[b]	48.76	—	−0.5304	—	11.76	—	−0.3692	0.054[c]

[a] Determined from the results of CULBERSON and PYTKOWICZ (1968).
[b] From the work of INGLE (1975). Valid only at $S = 35$ and for calcite. The value of $-\Delta V_A$ should be 2.8 cm/mole lower and ΔK_A can be assumed to be equal to ΔK_C.
[c] The σ at 25°C (0.032) is 2.3 times lower than the value at 2°C (0.072).

where ΔV_i and ΔK_i are the volume and compressibility change for the ionization. The values of ΔV_i and ΔK_i have been fit to equations of the form

$$-\Delta V_i = a_0 + a_1(S-34.8) + a_2 t + a_3 t^2 \quad (7a)$$

$$-10^3\,\Delta K_i = b_0 + b_1(S-34.8) + b_2 t + \ldots \quad (7b)$$

Coefficients of these equations generated from the results of CULBERSON and PYTKOWICZ (1968) are given in Table 5. Results obtained from the work of INGLE (1975) for the solubility of calcite are also given in Table 5.

As discussed elsewhere (MILLERO and BERNER, 1972; WARD and MILLERO, 1975) the values of ΔV_i for the ionization of boric and carbonic acids determined from molal volume measurements are in good agreement with those generated from the work of CULBERSON and PYTKOWICZ (1968) (see Table 6). Values of ΔK_i for the ionization of boric and carbonic acids determined from the measurements of CULBERSON and PYTKOWICZ (1968) are also in good agreement (Table 6) with the values calculated from partial molal compressibility data (MILLERO, 1979a). No attempt was made to force the seawater of ΔV_i and ΔK_i to the pure water values because direct measurements are not available at low salinities and molal volume calculations (MILLERO *et al.*, 1972; WARD and MILLERO, 1974) indicate that ΔV_i and ΔK_i are strongly dependent on concentration in dilute solutions. The coefficients a_1 and b_1 were obtained from $S = 38.5‰$ and 13.5°C results of CULBERSON and PYTKOWICZ (1968).

The values of ΔV_C and ΔK_C for the solubility of calcite in seawater are in reasonable agreement with the values determined from molal volume data (MILLERO, 1976, 1979b). The value of $-\Delta V_C = 31.8 \pm 1.0\,cm^3\,mol^{-1}$ determined for foraminifera at 25°C by PYTKOWICZ and FOWLER (1967) is $\sim 5.0\,cm^3\,mol^{-1}$ higher than the value obtained by INGLE (1975). These differences are probably related to differences in the solid phases. The ΔV_A for the solubility of aragonite should be $2.8\,cm^3\,mol^{-1}$ lower and ΔK_A should be approximately equal to ΔK_C (CRC CHEMICAL HANDBOOK, 1975). The value of ΔV_A determined in this manner does not agree with the measurements of INGLE (1973) and HAWLEY and PYTKOWICZ (1969) for oolites at 2°C. The work of Pytkowicz and coworkers yields a ΔV difference of $2.9\,cm^3\,mol^{-1}$ for foraminefera and oolites at 2°C while the work of Ingle yields a difference of $10.5\,cm^3$ mol for calcite and oolites. Part of this difference could be due to the larger temperature coefficient found by INGLE (1975) for calcite compared with the value found by HAWLEY and PYTKOWICZ (1969) for oolites. Further measurements are needed to elucidate these apparent discrepancies. Until this is done the effect of pressure on the solubility of calcite and aragonite can be estimated from the results given in Table 5.

CALCULATION OF PARAMETERS FOR THE CARBONATE SYSTEM IN SEAWATER

The various components of the carbonate system in seawater can be characterized by measuring at least two of the following: pH, A_T, ΣCO_2 and P_{CO_2}. The equations relating the selected parameters to the concentration of HCO_3^-, CO_3^{2-}, $CO_2^* = CO_2 + H_2CO_3$ are given by SKIRROW (1975). The classical way of determining the components of the carbonate system is to make measurements of the pH and total titration alkalinity, A_T, given by

$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+] + \sum_i B^- \quad (8)$$

where $[B(OH)_4^-]$, $[OH^-]$, $[H^+]$ are, respectively, the total concentrations of borate ion, hydroxide ion and the proton, and $\sum_i B^-$ represents other bases in seawater that can accept a proton ($H_2PO_4^{2-}$, PO_4^{3-}, etc., EDMOND, 1970). At the pH of natural seawater the carbonate alkalinity (A_C) can be determined from

$$A_C = A_T - [B(OH)_4^-] = [HCO_3^-] + 2[CO_3^{2-}]. \quad (9)$$

The concentration of the borate ion can be determined from

$$[B(OH)_4] = K'_B[B]_T/(K'_B + a_H) \quad (10)$$

where the total boron, $[B]_T = 1.212 \times 10^{-2}\,S$ (CULKIN, 1965), K'_B is the apparent composition constant for boric acid, and a_H is the apparent activity of the proton. From the pH and A_C the parameter of the

Table 6. Comparisons of ΔV and ΔK for boric and carbonic acids in seawater at 25°C determined from direct measurements and molal volume data

Solute	$-\Delta V$ (cm^3 mol^{-1}) Meas	Calc	$-\Delta K\,10^3$ (cm^3 mol^{-1} atm^{-1}) Meas	Calc[e]
$B(OH)_3$	27.1	25.7[a]	2.8	2.9
H_2CO_3	22.3	21.7[b]	0.9	1.7
HCO_3^-	15.4	15.9[c]	2.4	3.6
$CaCO_3(S)$	35.5	39.7[d]	2.5	8.2

[a] From WARD and MILLERO (1975). A higher value of $-\Delta V = 26.4$ cm^3 mol^{-1} is obtained for 0.725 m NaCl.
[b] From MILLERO and BERNER (1972) using $\bar{V}(H_2O) = 18.1$ cm^3 mol^{-1} instead of the value of 18.8 used in the original paper.
[c] From MILLERO and BERNER (1972) using $\bar{V}(CO_3^{2-}) = 19.2$ cm^3 mol^{-1} (DUEDALL, 1972).
[d] From $\bar{K}$ data of MILLERO (1979a).
[e] From MILLERO (1976).

carbonate system are determined from

$$[HCO_3^-] = A_C/[1 + 2K_2'/a_H] \qquad (11)$$

$$[CO_3^{2-}] = A_C K_2'/(a_H + 2K_2') \qquad (12)$$

$$[CO_2^*] = (A_C a_H/K_1')/(1 + 2K_2'/a_H) \qquad (13)$$

$$\Sigma CO_2 = [HCO_3^-] + [CO_3^{2-}] + [CO_2] = A_C(1 + a_H/K_1' + K_2'/a_H)/(1 + 2K_2'/a_H) \qquad (14)$$

where the values of K_i' are the apparent constants for carbonic acid. The values of K_i' and a_H used in these equations are for the *in situ* temperature and pressure of sample. The effect of temperature, pressure and salinity on the apparent constants were given earlier. The effect of temperature, pressure and salinity on the pH needed to calculate *in situ* values of a_H can be determined in two ways: (1) an iterative computer technique, and (2) by using explicit function of pH as a function of S, T and P. The iterative method (EDMOND and GIESKES, 1970) requires the solving of the cubic equation (SKIRROW, 1975).

$$a_H^3 + a_H^2[K_1'(A - 1) + K_B'(A - B)]/A + a_H[K_1'K_B'(A - B - 1) + K_1'K_2'(A - 2)]/A + K_1'K_2'K_B'(A - B - 2)/A = 0 \qquad (15)$$

which is derived by combining eqns (10) to (14). The values of A and B in eqn (15) are given by

$$A = A_T/\Sigma CO_2 \qquad (16)$$

$$B = [B]_T/\Sigma CO_2. \qquad (17)$$

Values of A and B are first estimated from eqns (8) to (12) using the measured a_H and the *in situ* apparent constants. Equation (15) is solved for a_H using the solutions for a cubic equation (CRC CHEMICAL HANDBOOK, 1975) or by iterative solutions (BEN-YAAKOV, 1970; ALMGREN *et al.*, 1975). Once the *in situ* a_H is determined the various parameters of the carbonate system can be determined from eqns (8) to (12). Since many workers do not have computer systems available, we have generated values of pH from eqn (15) as a function of temperature, pressure and salinity. The values have been generated using the constants of Hansson and Mehrbach *et al.* The effect of temperature and pressure on the pH_{NBS} are shown in Fig. 9. The effect of salinity on the temperature coefficients from $S = 30$ to $40‰$ is quite small and can be neglected. The least squares fit of the generated values of pH on the NBS and Tris scales are given by

NSB Scale

$$pH_t = pH_{25} + A(t - 25) + B(t - 25)^2 \qquad (18)$$

$$10^3 A = -9.702 - 2.378\,(pH_{25} - 8) + 3.885\,(pH_{25} - 8)^2 \qquad (18a)$$

$$10^4 B = 1.123 - 0.003\,(pH_{25} - 8) + 0.933\,(pH_{25} - 8)^2 \qquad (18b)$$

$$(\sigma = 0.002)$$

Tris Scale

$$pH_t = pH_{25} + A(t - 25) + B(t - 25)^2 \qquad (19)$$

$$10^3 A = -9.296 + 32.505\,(pH_{25} - 8) + 63.806\,(pH_{25} - 8)^2 \qquad (19a)$$

$$10^4 B = 3.916 + 23.000\,(pH_{25} - 8) + 41.637\,(pH_{25} - 8)^2 \qquad (19b)$$

$$(\sigma = 0.003)$$

where pH_{25} is the measured pH at t = 25 C. These equations are valid from t = 0–40 C, $S = 30$–$40‰$ and $pH_{25} = 7.6$–8.2. The generated values of pH have also been used to relate the two scales at various temperatures

$$pH_{NBS} = pH_{Tris} + A + Bt \qquad (20)$$

$$10^3 A = 5.93 - 3.6(S - 35) \qquad (20a)$$

$$10^3 B = 3.381 + 0.058(S - 35) \qquad (20b)$$

The differences between the two buffer scales are

Table 7. Comparisons of the pH_{NBS} and pH_{Tris} scales in seawater

Temp	$S = 30$ ΔpH	$S = 35$ ΔpH[a]	$S = 40$ ΔpH
0°C	0.073	0.057	0.038
5	0.092	0.077	0.059
10	0.109	0.095	0.079
15	0.125	0.113	0.099
20	0.141	0.130	0.117
25	0.156	0.147 (0.159)†	0.136
30	0.170	0.162	0.153
35	0.184	0.178	0.169
40	0.198	0.192	0.185

[a] $\Delta pH = pH_{NBS} - pH_{Tris}$.
† Experimentally measured by HANSSON.

given in Table 7. The calculated value of $pH_{NBS} - pH_{Tris} = 0.147$ at 25°C and $S = 35$ is in reasonable agreement with the directly measured values of 0.159 by HANSSON (1973). Further measurements as a function of salinity and temperature are needed to confirm eqn (20). The effect of applied pressure on the pH (NBS scale) of seawater is a linear function

$$pH_t^P = pH_t^0 + AP \tag{21}$$

The slopes are functions of t and S. A least squares fit of the generated values of $pH^P - pH^0$ give

$$-10^3 A = 0.424 - 0.0048(S - 35) - 0.00282t - 0.0816(pH^0 - 8) \tag{21a}$$

which is valid from $S = 32$–38 and t = 0–25°C.

A comparison of the various parameters of the carbonate system calculated from the apparent constants based on the two pH scales are given in Table 8. These calculations were made at $t = 25$°C and $S = 35‰$ for waters of the same $A_T = 2.400$ m-equiv kg^{-1} and $\Sigma CO_2 = 2.111$ mmol kg^{-1}. The differences of K_B determined from the results of LYMAN (1957) and HANSSON (1973) cause a difference in $[B(OH)_4^-]$ of 0.011 m-equiv kg^{-1}. This difference is larger than what one would expect (0.004) from the standard errors in $\ln K_B'$. Until these discrepancies are clarified, it is not possible to determine the carbonate alkalinity, A_C, to better than ±0.01 m-eqiv kg^{-1}. The differences in $[HCO_3^-]$ and $[CO_3^{2-}]$ are 0.010 mmol kg^{-1}. For waters with the same A_C (the values in parentheses in Table 8) the difference in $[HCO_3^-]$ increases to 0.019 mmol kg^{-1}, while the difference in $[CO_3^{2-}]$ is nearly the same (0.009 mmol kg^{-1}). These differences in $[HCO_3^-]$ and $[CO_3^{2-}]$ are about what one would expect from the standard errors obtained from the constants of HANSSON (1972) and MEHRBACH *et al.* (1973). The calculated values of $[CO_2^*]$ and P_{CO_2} using the two sets of apparent constants are in good agreement and within the expected errors due to the standard errors of K_1' and K_2'. These calculations indicate that the presently available apparent constants expressed on the NBS and Tris pH scales cause maximum differences of $\delta A_C = 0.011$ m-equiv kg^{-1}, $\delta[HCO_3^-] = 0.019$ mmol kg^{-1}, $\delta[CO_3^{2-}] = 0.010$ mmol kg^{-1}, $\delta[CO_2^*] = 0.0001$ mmol kg^{-1}, and $\delta P_{CO_2} = 4 \times 10^{-6}$ atm. It is interesting to compare the errors due to the apparent constants to those obtained from the experimental errors in pH, A_T and ΣCO_2. The precision of the measurements of these parameters are ±0.003 in pH (PYTKOWICZ *et al.*, 1966; ZIRINO, 1975); ±0.002 m-equiv kg^{-1} in A_T (HANSSON, 1972; ALMGREN and FONSELIUS, 1976) and ±0.003 mmol kg^{-1} in ΣCO_2 (HANSSON, 1972; ALMGREN and FONSELIUS, 1976). The errors of various parameters of the carbonate system due to experimental measurements of pH and A_T or A_T and ΣCO_2 are given in Table 9. The uncertainty in the various carbonate parameters due to experimental errors are within the errors due to the apparent constants, except for the errors in P_{CO_2} (due to errors in ΣCO_2). If one set of constants are used the errors become comparable except for HCO_3^- and CO_3^{2-}. To improve our ability

Table 8. Comparisons of the parameters of the carbonate system determined at 25 C and $S = 35$ using various pH scales[a]

Parameter	NBS Scale	Tris Scale	Δ[b]
A_T, m-equiv kg^{-1}	2.400	2.400	0
ΣCO_2, 10^6 mmol kg^{-1}	2.111	2.111	0
pH	8.151	8.007	0.144
$B(OH)_4^-$	0.095 ± 0.003	0.084 ± 0.001	0.011 ± 0.003
A_C, m-equiv kg^{-1}	2.305 ± 0.003	2.316 ± 0.001 (2.305 ± 0.001)	0.011 ± 0.003
$[HCO_3^-]$, mmol kg^{-1}	1.890 ± 0.011	1.880 ± 0.014 (1.871 ± 0.018)	0.010 ± 0.018 (0.019 ± 0.018)
$[CO_3^{2-}]$, mmol kg^{-1}	0.208 ± 0.005	0.218 ± 0.007 (0.217 ± 0.007)	0.010 ± 0.009 (0.009 ± 0.009)
$[CO_2^*]$, mmol kg^{-1}	0.01340 ± 0.0002	0.01347 ± 0.0004 (0.0130 ± 0.0004)	0.00003 ± 0.0004 (0.0001 ± 0.0004)
P_{CO_2}, 10^6 atm	472 ± 7[c]	471 ± 14 (468 ± 14)	1 ± 16 (4 ± 16)

[a] The errors are only related to the errors in the apparent constants.
[b] The ± deviations have been determined from $(\Delta_1^2 + \Delta_2^2)^{1/2}$.
[c] Calculated using the Henry's law α from WEISS (1974).

Table 9. Comparisons of the experimental errors in the values of parameters for the carbonate system with errors due to the apparent constants

Parameter	From pH and A_T ΔpH^a	ΔA_T^b	From A_T and ΣCO_2 ΔA_T^b	$\Delta \Sigma CO_2^c$	From constants[d]
$B(OH)_4^-$, m-equiv kg^{-1}	0.0005	—	0.003	0.001	0.011
A_C, m-equiv kg^{-1}	0.0005	0.002	0.001	0.001	0.011
$[HCO_3^-]$, mmol kg^{-1}	0.002	0.002	0.001	0.005	0.010
$[CO_3^{2-}]$, mmol kg^{-1}	0.002	0.001	0.001	0.002	0.011
$[CO_2^*]$, mmol kg^{-1}	0.0001	0.0001	0.0001	0.0002	0.0002
P_{CO_2}, 10^6 atm	4	1	3	7	4
ΣCO_2, 10^6 mmol kg^{-1}	0.001	0.002	—	—	—
ΔpH	—	—	0.003	0.005	—

[a] Error due to $\delta pH = \pm 0.003$ (pH = 8.15 and $A_T = 2.4$).
[b] Error due to $\delta A_T = \pm 0.002$ (pH = 8.15 and $A_T = 2.4$).
[c] Error due to $\delta \Sigma CO_2 = \pm 0.003$ ($A_T = 2.4$ and $\Sigma CO_2 = 2.111$).
[d] The maximum errors related to the uncertainty of the apparent constants on NBS and Tris scales.

to calculate reliable values of HCO_3^- and CO_3^{2-}, it will be necessary to make new measurements on K_2'. The experimental errors in determining ΣCO_2 result in larger errors in HCO_3^- and P_{CO_2} than one might desire. This results in an uncertainty of ~0.005 in pH which is slightly larger than the precision of pH measurements (PYTKOWICZ *et al.*, 1966; ZIRINO, 1975). Until the precision in the determination of ΣCO_2 obtained by a computer titration improves, pH measurements should be made. This can be done by periodic calibration of the electrode system and using the initial emf reading in the computer titration (ALMGREN and FONSELIUS, 1976). Although the experimental precision of determining pH, A_T and ΣCO_2 using computer assisted titrations is quite high, the accuracy is difficult to evaluate. The results of the GEOSECS intercalibration work (TAKAHASHI *et al.*, 1970) point out the need of standards in carbonate studies of seawater.

The saturation state, Ω, of calcite and aragonite in seawater can be determined from

$$\Omega = [Ca][CO_3]/K_{sp}' \tag{22}$$

where $[Ca] = 2.938 \times 10^{-4}\, S$ mol kg^{-1} (MILLERO, 1979c) and K_{sp}' is the solubility product of calcite or aragonite at the *in situ* t, P and *S*. The values of K_{sp}' fit in this study are based on the carbonate constants of MEHRBACH *et al.* (1973). An error of ± 0.005 mmol kg^{-1} in $[CO_3]^{2-}$ yields an error of ± 0.11 in Ω_C (2.3%) and ± 0.08 in Ω_A (2.5%). Errors in K_{sp}' at 1 atm yield errors of ± 0.32 in Ω_C (6.7%) and ± 0.21 in Ω_A (6.6%). From these calculations it is apparent that the largest source of errors in determining Ω are due to uncertainties in the apparent constants for the solubility of $CaCO_3$. The calculation of Ω in deep waters has the added uncertainty due to the effect of pressure on K_{sp}'. The pressure coefficients of INGLE (1975) cause an uncertainty in Ω_C of ~ ±1.0% per km. The differences between the pressure coefficients of PYTKOWICZ and FOWLER (1967) and INGLE (1975) for calcite cause a larger uncertainty in Ω_C of ~2.4% per km. Further measurements are needed to clear up these apparent discrepancies.

To summarize, I have attempted to provide a statistically valid representation of the apparent ionization constants of water, boric and carbonic acids, and the solubility of $CaCO_3$ in seawater as a function of t, *S* and P. At present, I feel that the apparent constants on the NBS pH scale (LYMAN, 1957; MEHRBACH *et al.*, 1973; INGLE *et al.*, 1973, 1975; CULBERSON and PYTKOWICZ, 1968) should be used to characterize the parameters of the carbonate system in seawater. Further measurements for all of the constants are needed below $S = 20‰$ as well as measurements for K_B' from $S = 20$–$40‰$ on the NBS scale. High pressure measurements on the solubility of various forms of $CaCO_3$ are also needed.

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